The Spectrum of Ionised Potassium.

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[Plate 6.]

In 1904 Eder and Valenta* found that potassium, under the excitation of a sharp spark discharge, could be made to emit, in addition to the ordinary arc series spectrum, a new one, which was rich in wave-lengths and which extended into the ultra-violet. In 1907, Goldstein† found this spectrum could, when special experimental arrangements were adopted, be obtained pure and unmixed with any of the wave-lengths of the arc spectrum. To it he gave the name the "ground spectrum" of potassium.

In his paper Goldstein gives the values of the wave-lengths of a few of the constituents of this spectrum, but as the discharge tubes used by him were made of glass, his list of wave-lengths did not extend beyond the visible.

In 1909 a further study of this "ground spectrum" was made by Schillinger‡, and the wave-lengths were determined by him not only in the visible region but also in the violet and the ultra-violet region as far as $\lambda = 2144 \cdot 6$ Å.U.

In 1915 some observations were also made by Edgar H. Nelthorpe§ on the "ground spectra" of the alkali and alkaline earth metals, in which the wave-lengths for potassium were measured from $\lambda = 6307$ Å.U. to $\lambda = 3897 \cdot 9$ Å.U.

Recently Sommerfeld|| has revived interest in this spectrum through his pointing out that the configurations of the extra-nuclear electron systems of the positive ions of the alkali metals are, on the basis of the views which are commonly held at present regarding the structure of atoms, likely to be identical with the configurations of the extra-nuclear electron systems of the atoms of the rare gases. This will be made evident by the representations of atomic structure given in fig. 1.

From these it will be seen that the number of the extra nuclear electrons associated with the atoms of the various elements cited is determined by the atomic numbers of these elements. Moreover, the atoms of the alkali metals are similar in that they all have but one electron in their outside ring.

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[*] Eder and Valenta, 'Denkschr. Wien. Akad.,' vol. 61, p. 347 (1894).

[†] Goldstein, 'Verh. d. Deut. Phys. Ges.,' vol. 9, p. 321 (1907).

[‡] Schillinger, 'Wien. Ber.,' vol. 118, IIa, p. 266 (1909).

[§] Nelthorpe, 'Ast. Phys. Jour.,' No. 41, p. 16 (1915).

[||] Sommerfeld, 'Atombau und Spektrallinien,' p. 296.

Their similarity in this respect is paralleled by the fact that in the arc spectra of the alkali elements the wave-lengths can be grouped into doublet series which are the same in number and the same in type for all the elements in the alkali group. Going one step further, Sommerfeld has emphasised the view that these doublet series of wave-lengths in the spectra of the alkali elements have their origin in the outside ring electron of the atoms of the respective elements.

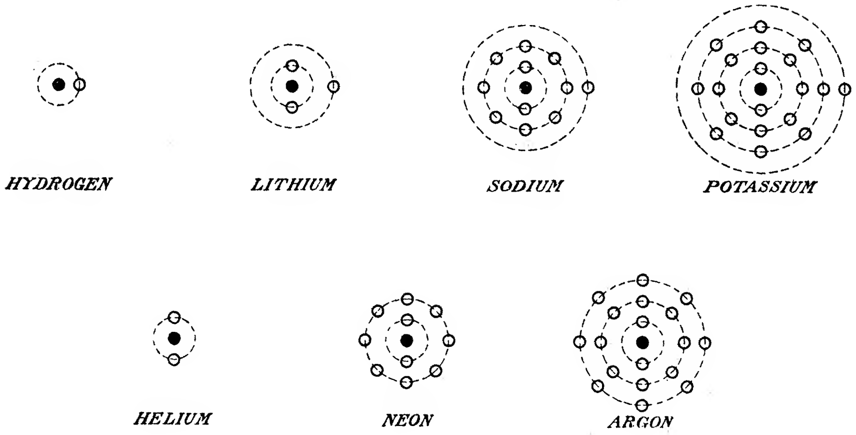

Fig. 1.

When an element of the alkali group is subjected to spark excitation, it is assumed that the violence of the disturbance to which the atoms are subjected is so great that the outer electron is removed entirely from these atoms and that the radiations which are emitted by them under these circumstances must have their origin in the electrons still remaining. Such radiations would constitute the so-called enhanced spectra. Taking potassium, for example, it will be seen that when the outer electrons are removed from the atoms of this element, the configuration of the electrons still remaining is identical with the extra-nuclear electron system of an ordinary atom of argon. It follows, then, that the enhanced spectrum of potassium should be identical in type with the ordinary arc spectrum of argon.* The only difference between the two spectra would be that in the case of potassium, where the nuclear charge is one unit higher than that of argon, the enhanced spectrum might be expected to appear farther down in the violet or ultra-violet region.

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* [*Footnote added September* 20, 1921.—It may be that the ordinary spectra of argon can be obtained as well from an electric discharge in the gases and vapours obtainable from heated potassium. This element and rubidium are known to be radioactive. They emit beta-rays and possibly, too, alpha-rays. The emission of such radiations would indicate the possibility of potassium being transmuted into argon and of rubidium into krypton.]

Now argon is known to be capable of emitting two types of spectrum, the one known as the red spectrum, which is produced under conditions of moderate excitation, and the other the blue spectrum, emitted when violent or intense stimulation is used. From this it follows that it should be possible to cause the atom of potassium to emit three definite and distinct types of spectrum. The first would be the ordinary arc spectrum of the element—the spectrum which constitutes the doublet system; the second would correspond with and be similar to the red spectrum of argon; and the third would represent the blue spectrum of this element. The first would be the result of moderate excitation, the second of more or less intense excitation, and the third would probably be obtained when the stimulation was extremely violent.

From the considerations presented above it seems clear that we have in the "ground spectrum" of potassium, discovered by Eder and Valenta, the enhanced spectrum of that element. Moreover, if the views put forward by Sommerfeld be correct, it would follow that the enhanced spectrum should possess characteristics identical with those of the red spectrum of argon, and possibly, too, if the excitation used were sufficiently intense, of the blue spectrum.

The present investigation was begun with the object of putting these views to the test. It was intended to do so by calculating the ratios of the frequencies of the wave-lengths in the red and blue spectra of argon and by comparing them with the ratios of the frequencies of the wave-lengths of the enhanced spectrum of potassium, using Schillinger's results for the calculation of the latter. But prior to this enquiry, some observations were made on the enhanced spectrum of potassium, in the course of which it was found that a great many wave-lengths came out on the plates which had not been observed by Schillinger. The original programme was therefore deferred for a time, and an effort was made to obtain as complete a record as possible of the wave-lengths of the radiations emitted by potassium under intense excitation. The results of this part of the investigation are given below.

1. *Mode of Excitation.*

Various types of arcs in potassium vapour with high potential differences applied to the electrodes were tested, but with none of them was the enhanced spectrum far down in the ultra-violet region obtained. The spark discharge in air proved equally unsatisfactory in this respect.

When, however, a very powerful electrodeless discharge was used with potassium vapour of low density, the enhanced spectrum came out strongly and clearly. In obtaining the electrodeless discharge, a 12-inch induction coil was used, with its secondary joined in parallel with two sets of four Leyden jars, each having a volume of about one gallon.

The coil was operated with a Wehnelt interrupter joined to the 110 D.C. mains. Pyrex glass bulbs about 9 cm. in diameter were used for holding the potassium, and these were provided with a side tube closed by a fluorite window when the ultra-violet spectrum was being photographed with quartz and fluorite spectrographs.

Prior to introducing the potassium into the bulbs the latter were thoroughly exhausted, and during the exhaustion they were heated to about 400° C. in order to drive out any gases occluded in their walls. The potassium was distilled into the bulbs from a side tube which was sealed off after sufficient potassium had been introduced. In working with a vacuum grating spectrograph, the side tube of the pyrex glass bulbs was used without the fluorite

Table I.—List of Wave-lengths obtained by Author in region between $\lambda = 6950$ Å.U. and $\lambda = 3489$ Å.U., with electrodeless discharge in potassium vapour, in addition to those obtained by Schillinger* for the same spectral region with the spark discharge.

Intensity.	Wave-length.	Remarks.
	λ (Å.U.).	
3	6050	
2	5730	
1	4958	Ramage,† 4957; Kayser and Runge‡, 4956·8.
3	4863	Liveing and Dewar,§ 4863·8; Ramage, 4862.
1	4805	Liveing and Dewar, 4803·8.
1	4790	Liveing and Dewar, 4788·8.
1	4769	Ramage, 4767.
1	4760	Liveing and Dewar, 4759·8.
1	4744	
1	4720	
1	4688	
1	4643	Saunders, 4642·5.‖
2	4454	
2	4365	
1	4103	
3	3660	
4	3660	
1	3590	
1	3583	
1	3572	
1	3489	

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* Schillinger, 'Wien. Ber.,' vol. 118, IIA, p. 266 (1909)

† Ramage, 'Roy. Soc. Proc.,' vol. 70, p. 304 (1902).

‡ Kayser and Runge, 'Spectroscopie,' vol. 5, p. 635 (1910).

§ Liveing and Dewar, 'Roy. Soc. Proc.,' vol. 29, p. 398 (1879).

‖ Saunders, 'Ast. Phys. Jour.,' vol. 20, p. 183 (1904).

Table II.—Ultra-Violet Spectrum of Potassium (Electrodeless Discharge).

Author.		Schillinger (spark discharge).	
Intensity.	Wave-length.	Intensity.	Wave-length.
	λ (Å.U.).		λ (Å.U.).
6	3345·8	5	3345·8
3	3336·7		
3	3324·65		
		4	3322·46
5	3312·7	4	3312·77
3	3303·5		
5	3292·25	3	3291·07
3	3279·1	3	3278·84
3	3262·5	2	3262·02
3	3257·4		
3	3244·5		
		2	3241·14
1	3223·7	1	3224·66
0	3220·0	2	3220·93
		1	3218 87
		1	3217·54
0	3213·0		
		4	3209·45
4	3205·6		
		3	3202·09
5	3189·0	2	3190·55
		2	3188·04
2	3174·0		
4	3171·9	1	3170·02
3	3159·4		
		1	3157·62
2	3148·6		
4	3130·6	2	3129·52
		4	3105·43
6	3104·3		
		1	3103·05
2	3076·95		
		1	3074·55
5	3062·15	5	3062·56
0	3057·0	2	3056·96
2	3052·85	3	3052·17
2	3048·6		
3	3031·6	1	3030·79
3	3024·8	2	3023·56
3	2993·4	3	2992·47
2	2985·9	1	2986·05
1	2966·9		
		1	2963·37
1	2955·8		
2	2939·5	1	2938·55
1	2926·8		
2	2904·9		
2	2855·7	1	2854·06
3	2836·2		
		1	2833·25
2	2825·7		
3	2819·6	1	2819·24
5	2803·8		
		1	2780·2
1	2778·0		
1	2768·1		
2	2742·8	1	2743·5

Table II.—(*contd.*).

Author.		Schillinger (spark discharge).	
Intensity.	Wave-length.	Intensity.	Wave-length.
	λ (Å.U.).		λ (Å.U.).
4	2735·6	1	2736·1
1	2732·0		
3	2689·1	1	2690·5
3	2661·1		
1	2655·8		
		1	2635·7
4	2633·9		
0	2630·0		
2	2612·9	1	2614·2
1	2569·8		
2	2559·2		
4	2549·6	1	2549·6
		1	2538·7
3	2536·0		
2	2502·4		
3	2475·6	1	2474·3
3	2470·4		
2	2451·25		
4	2446·0		
2	2440·9	1	2440·7
4	2436·6		
3	2410·4		
3	2402·0		
3	2393·4		
		1	2379·6
4	2376·3		
5	2370·25		
2	2365·8		
7	2362·6		
		1	2358·9
3	2351·9	1	2350·3
4	2348·3		
3	2343·2	1	2343·2
3	2340·15		
0	2335·0		
0	2332·0		
2	2328·27	1	2328·0
3	2324·33		
5	2319·15		
4	2315·22		
0	2312·0	1	2311·7
0	2309·0		
3	2306·58		
1	2304·0		
3	2300·9		
2	2295·16		
0	2290·0		
2	2284·32		
3	2280·05		
0	2273·0	1	2274·2
5	2270·9		
5	2265·04		
		1	2262·2
3	2262·0	1	2261·8
5	2260·32	1	2260·7
		1	2257·9
3	2255·29	1	2255·0

Table II.—(*contd.*).

Author.		Schillinger (spark discharge).	
Intensity.	Wave-length.	Intensity.	Wave-length.
	λ (Å.U.).		λ (A.U.).
2	2253·0		
5	2250·92		
0	2248·0	1	2248·2
2	2246·32		
2	2243·0		
6	2240·89		
0	2237·0		
2	2231·67		
2	2226·0		
5	2221·58		
3	2217·23		
4	2213·1		
4	2210·53		
4	2206·28	1	2205·2
0	2203·0	1	2203·7
2	2200·89		
3	2194·89	1	2196·8
6	2190·0		
6	2186·93		
1	2182·4		
3	2177·92		
3	2175·12		
2	2171·03		
1	2163·31		
0	2159·0		
4	2155·3		
0	2152·0		
3	2149·42		
7	2143·9	1	2144·6
1	2141·0		
1	2140·49		
5	2137·56		
3	2132·8		
4	2130·75		
4	2128·9		
4	2127·25		
4	2122·0		
3	2114·2		
3	2110·05		
1	2105·45		
0	2102·0		
1	2101·05		
3	2100·0		
3	2097·65		
2	2093·3		
6	2089·8		
4	2085·2		
3	2082·1		
10	2077·9		
0	2071·0		
2	2070·0		
1	2067·2		
2	2062·05		
4	2054·9		
1	2053·1		
2	2049·8		
1	2045·7		

Table II.—(*contd.*).

Author.		Schillinger (spark discharge).	
Intensity.	Wave-length.	Intensity.	Wave-length.
	λ (Å.U.).		λ (Å.U.).
1	2043·1		
6	2036·9		
1	2027·8		
1	2019·6		
2	2010·7		
2	2006·8		
2	1999·2		
4	1995·1		
3	1981·6		
3	1976·4		
1	1974·7		
2	1965·1		
2	1960·2		
2	1952·6		
5	1944·6		
1	1940·9		
3	1933·5		
1	1930·8		
1	1926·3		
2	1923·8		
2	1921·4		
1	1908·4		
1	1905·9		
1	1904·5		
2	1902·8		
1	1897·8		
2	1894·8		
1	1892·5		
1	1891·7		
2	1890·6		
1	1873·9		
2	1873·3		

window and was attached directly to the spectrograph so as to permit the slit of the latter to be strongly and directly illuminated by the radiation emitted by the discharge in the bulb.

2. *Results.*

Reproductions of the photographs of the spectra obtained with small and large quartz spectrographs of the Hilger type are shown in Plate 6, and the mean values of the wave-lengths obtained from measurements on a number of photographic plates are given in Tables I and II. The values given in Table I are to be considered as correct to one-half an Ångström unit.

From the Tables it will be seen that over 150 wave-lengths were recorded in addition to those previously observed by Schillinger.

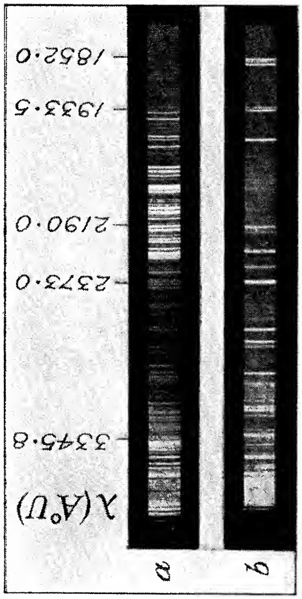
In photographing the spectrum with a vacuum grating spectrograph wave-lengths were recorded at $\lambda = 1742{\cdot}2$, 1493·4, 1395·4, 1199·7, 1135·0 and

1085·3 Å.U. Of these wave-lengths $\lambda = 1742\cdot2$ Å.U. may possibly belong to the spectrum of potassium. The remaining five came out with strong intensity on numerous occasions when photographing the spectrum of helium. Some difficulty has been experienced in fixing the identity of these wave-lengths, though there are indications that some, at least, of them may have originated in the atoms of mercury through a slight diffusion of the vapour of this element from a Langmuir condensation pump which was used in conjunction with a set of Trimount oil pumps to evacuate the spectrographs.

From the reproductions of the enhanced spectrum of potassium shown in the Plate it will be seen that the wave-lengths, from the point of view of numbers and intensity, fall roughly into two divisions with a certain amount of overlapping. In the one division the "optical" or "spectral" centre of gravity is approximately at $\lambda = 3800$ Å.U. and in the other it is in the neighbourhood of $\lambda = 2100$ Å.U. This suggests that we have here spectra which are analogous to the ordinary and enhanced spectra of argon, the one with its spectral centre of gravity at $\lambda = 3800$ Å.U., corresponding to the red spectrum of argon, and the other with its spectral centre of gravity at $\lambda = 2100$ Å.U., corresponding to the blue spectrum of this element.

It is proposed to make an analysis of the frequencies of the wave-lengths recorded in the Tables and of the additional ones given by Schillinger in order to see if this parallelism can be established numerically. If such a numerical parallelism can be established it will constitute a definite confirmation of the view put forward by Sommerfeld.

In concluding, I wish to express my thanks to my assistants, Messrs. P. A. Petrie and P. Blackman, for helping me to take the photographs, and to Mr. Vladimir Lubowich and several of my students, for measuring the plates and checking the results for me.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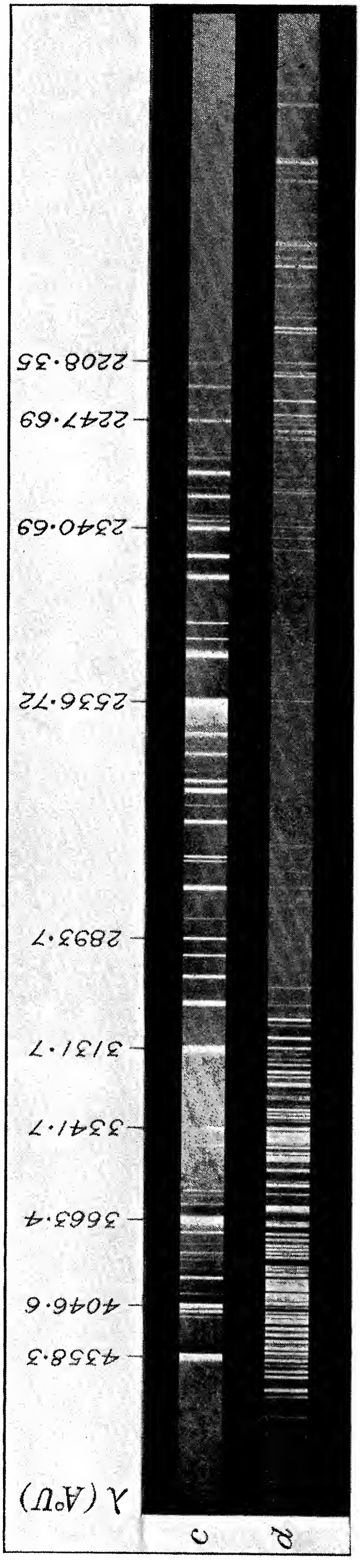
1933·5
2190·0
2373·0
3345·8
λ (A°U)
a
b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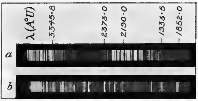
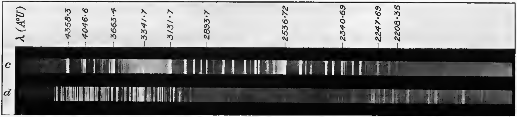
2247·69
2340·69
2536·72
2893·7
3131·7
3341·7
3663·4
4046·6
4358·3
λ (A°U)
c
d


λ (A°U)
3345·8
2373·0
2190·0
1933·5
1852·0
a
b


λ (A°U)
4358·3
4046·6
3663·4
3341·7
3131·7
2893·7
2536·72
2340·69
2247·69
2208·35
c
d